

What is claimed is:

1. Continuous process for the manufacture of methylmercaptan by contacting an intimate mixture of carbon oxides, sulfur or hydrogen sulfide and hydrogen 5 at elevated temperatures and pressures over a preformed solid catalyst comprising an active component of Mo-O-K-based species, an active promoter and, optionally, a carrier.
2. Process according to claim 1, wherein the active 10 component is a Mo-O-K-based species, its precursor are oxides of molybdenum.
3. Process according to claim 2, wherein the active component is a potassium molybdate or ammonium heptamolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ plus a potassium salt or 15 molybdenum oxide plus a potassium salt.
4. Process according to claim 3, wherein the weight ratio of K_2MoO_4 /carrier is of from 0.01-0.80/1, when the active component is expressed by the amount of K_2MoO_4 ; or the weight ratio of $\text{MoO}_3/\text{K}_2\text{O}$ /carrier is 0.01- 20 0.80/0.01-0.50/1, when the active component is expressed by the amount of MoO_3 and K_2O .
5. Process according to claim 1, 2, 3, or 4, wherein the active component of the catalyst is impregnated or 25 coated onto the carrier by multi-step impregnation applied to the surface of the support or coating of the support with the active component.
6. Process according to claim 1, 2, 3 or 4, wherein the active catalyst mass is extruded or pelletized to form three dimensional catalyst particles.
- 30 7. Process according to Claim 1, wherein the unreacted gas is recycled to the feed gas stream in the process.

8. Process according to claim 7, wherein the gas to be recycled is separated from all by-products which are liquid at 0-5°C and ambient pressure, and wherein the recycling gas is catalytically converted so as to only consist of carbon oxides, hydrogen and hydrogen sulfide.
9. Process according to any of the preceding claims, wherein the selectivity of each of the by-products methane, dimethylsulfide and carbon bisulfide is not higher than 1%.
10. Process according to any of the preceding claims, wherein the total selectivity of methylmercaptan can be increased by decreasing the total gas hourly space velocity to less than 10.000 h⁻¹, and/or by simultaneously increasing the reaction temperature to temperatures up to 500°C.
11. Process according to Claim 10, wherein the total gas hourly space velocity is decreased so as to be within the range of 100 h⁻¹ to 5000 h⁻¹, and/or the reaction temperature is simultaneously increased to temperatures from 250 to 400°C.
12. Process according to any of the preceding claims, wherein the total selectivity of methylmercaptan is increased by at least 1,5%, by decreasing the total gas hourly space velocity by 75%.
13. Process according to claim 1, wherein the carrier is silica.
14. Process according to claim 1, wherein the active promoter of said catalyst system is a mixture of oxides or sulfides or sulfides and oxides selected from the groups consisting of molybdenum, iron, cobalt, nickel, lanthanum, cerium and manganese.

15. Process according to claim 14, wherein the active promoter is selected from the group consisting of transition metal oxides or rare earth metal oxides.
16. Process according to claim 14, wherein the weight ratio of the contents in the catalyst $K_2MoO_4/M_xO_y/carrier$ equals to $0.01-0.80/0.01-0.10/1$, when the amount is expressed by M_xO_y ; or the weight ratio of the contents in the catalyst $MoO_3/K_2O/M_xO_y/carrier$ equals to $0.10-0.50/0.10-0.30/0.01-0.10/1$, wherein M is selected from the group consisting of transition metal oxides and rare-earth metal oxides, and x and y are integers from 1 to 5.
17. Process according to claim 16, wherein M is an oxide selected from the group consisting of iron, molybdenum, manganese, cobalt, nickel, lanthanum and cerium.
18. Process according to claim 3, wherein the active components are metal sulfides, produced by sulfurizing with hydrogen sulfide prior to the reaction.
- 20 19. The process according to claim 1, wherein the potassium component in the Mo-O-K is derived from the group consisting of potassium acetate, potassium oxalate, potassium hydroxide, potassium carbonate, potassium nitrate, and potassium bicarbonate.
- 25 20. Process according to claim 1, wherein the catalyst is prepared by multi-step impregnation when K_2MoO_4 , MoO_3 or $(NH_4)_6Mo_7O_24$ plus a potassium salt is employed as precursor of the active component.
21. Process according to claim 20, wherein impregnation is 30 performed by using potassium salts selected from the group consisting of potassium acetate, potassium oxalate, potassium hydroxide, potassium carbonate, potassium nitrate, and potassium bicarbonate, and

oxides or sulfides selected from the group consisting of molybdenum, iron, cobalt, nickel, lanthanum, cerium and manganese.

22. Process according to claim 1, wherein the reactor
5 temperature is at least 250°C, the total pressure is at least 2 bar, the total gas hourly space velocity ranges from 100 - 5000 h⁻¹ and the reactants are at a temperature of at least 120°C when fed to the reactor.

23. Process according to claim 1 or 20, wherein the
10 temperature is of from 300-450°C, the pressure is at least 4 bar and the total gas hourly space velocity is 750-3000 h⁻¹.

24. Process according to claim 1, wherein the reactants, carbon oxide, sulfur and or hydrogen sulfide and
15 hydrogen are fed to the reactor, respectively, at a proportion of 1/0/1/0 to 1/10/10/10.

25. The process of claim 6, wherein the reaction is carried out in a fixed catalyst bed arrangement or in
20 a fluidized bed to aid in reactor temperature control of the exothermic reaction.

26. Process according to claim 1 or 7, wherein a series of fixed catalyst beds or a reactor comprising one or
25 multiple (n = 1 - 10) reaction zones is used for the chemical reaction, in which one or more of the reacting gases can be fed between the reaction zones.

27. Process according to claim 1, wherein the catalyst may be arranged in fixed beds with intermediate gas injection or multitubular reactors for a better temperature control.

30 28. Process according claim 26, wherein hydrogen, hydrogen sulfide, synthesis gas, and/or carbon oxides are fed to the reaction mixture between the reaction zones.

29. Process according to claim 7 or 26, wherein all products which are liquid at 0-5°C and ambient pressure after the reaction are separated from the gas and the gas is then recycled into the remaining gaseous fraction to the feed gas.
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30. Process according to claim 29, wherein the recycling gas is directed over a catalyst bed for the conversion of by-products before being recycled to the feed gas stream.
- 10 31. Process according to claim 30, wherein the main by-products are carbonyl sulfide, carbon disulfide, and/or dimethylsulfide.
32. Process according to claim 30, wherein by-products are catalytically converted to carbon dioxide, methylmercaptan and hydrogen sulfide before recycling them to the feed gas stream.
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33. A process for preparing a solid, preformed catalyst system comprising the steps of
 - I) preparing an impregnation liquid of an aqueous solution of a salt of a transition metal or rare-earth metal and a precursor of K_2MoO_4 or $(NH_4)_6Mo_7O_24$ plus a potassium salt or MoO_3 plus a potassium salt; and
 - 20 II) impregnating a suitable carrier with such impregnation liquid, followed by drying the intermediate produced, and calcinating such intermediate to obtain the catalyst.
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 34. A process for preparing a solid, preformed catalyst system comprising the steps of

- A) preparing an impregnation liquid of an aqueous solution of a salt of a transition metal or rare-earth metal;
- 5 B) impregnating a suitable carrier with such impregnation liquid, followed by drying the intermediate produced, optionally calcinating such intermediate;
- 10 C) preparing an aqueous steeping solution of a precursor of K_2MoO_4 or $(NH_4)_6Mo_7O_24$ plus a potassium salt or MoO_3 plus a potassium salt; and
- D) steeping the intermediate produced in (B) with the aqueous steeping solution produced in (C) and then drying and calcinating the resultant catalyst.

15 35. Process according to claim 33 or 34, wherein the impregnation liquid and/or the steeping solution is treated with alkyl amides, or an organic acid containing at least one carbon atom and at least one acid function.

20 36. Process according to claim 35, wherein the alkyl amide is dimethylformamide or dimethyl acetamide, and the organic acid is formic acid, acetic acid, propionic acid, butyric acid, pentanoic acid, hexanoic acid, acrylic acid, propionic acid, vinylacetic acid, methacrylic acid, crotonic acid, 4-pentenoic acid, sorbonic acid, oxalic acid, malonic acid, succinic acid, maleic acid, 3-hydroxybutyric acid, glutaric acid, adipic acid, citric acid, tartaric acid or ethylene diamine-tetracetic acid.

25 37. Process according to claim 35 or 36, wherein the organic acid is citric acid.